phate of copper is added to a hot solution of tricarballylate of soda. It is insoluble in water, but soluble in dilute acids.

Tricarballylate of Lead, $\left.\begin{matrix} C_{12}H_5O_6''' \\ Pb_3 \end{matrix}\right\} O_6$.

This salt precipitates when an excess of acetate of lead is added to a solution of tricarballylate of soda. It is a white powder insoluble in water, but soluble in dilute nitric acid.

The composition of the foregoing salts and ethers fully confirms the view I took of the basicity of this acid in my preliminary paper. It is, I believe, at present the sole representative of its class. It will not, however, I believe, long remain so, as the process by which it has been obtained will, I have no doubt, be found to be of general application.

This acid bears the same relation to citric acid that succinic bears to malic acid:—

$C_{12}H_8O_{12}$, tricarballylic acid.	$C_8H_6O_8$, succinic acid.
$C_{12}H_8O_{14}$, citric acid.	$C_8H_6O_{10}$, malic acid.

That this relationship exists not only on paper, but also in the nature of the bodies themselves, is, I think, highly probable. In order to arrive at certainty on this point, I have endeavoured, by the addition of two equivalents of oxygen, to transform tricarballylic into citric acid. My researches in this direction have not hitherto been attended with success.

II. "Notes of Researches on the Acids of the Lactic Series.—No. III. Action of Zincethyl upon Ethylic Leucate." By E. Frankland, F.R.S., and B. F. Duppa, Esq. Received February 1, 1865.

In describing the production of ethylic leucate or diethoxalate*, formed when zincethyl acts upon ethylic oxalate, we assumed the intermediate formation of zincoleucic ether, and explained the reaction by the following equation, in which zinc is regarded as a monatomic metal:—

$$C_2\left\{\begin{matrix} O \\ O\,C_2H_5 \\ O \\ O\,C_2H_5 \end{matrix}\right. + Zn'_2\left\{\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right. = C_2\left\{\begin{matrix} (C_2H_5)_2 \\ OZn' \\ O \\ O\,C_2H_5 \end{matrix}\right. + \left.\begin{matrix} Zn' \\ C_2H_5 \end{matrix}\right\} O.$$

Ethylic oxalate. Zincethyl. Zincoleucic ether. Zincethylate.

In contact with water we conceived zincoleucic ether to be decomposed with the formation of ethylic leucate and zinc hydrate,

$$C_2\left\{\begin{matrix} (C_2H_5)_2 \\ OZn' \\ O \\ O\,C_2H_5 \end{matrix}\right. + H_2O = C_2\left\{\begin{matrix} (C_2H_5)_2 \\ OH \\ O \\ O\,C_2H_5 \end{matrix}\right. + \left.\begin{matrix} Zn' \\ H \end{matrix}\right\} O.$$

Zincoleucic ether. Ethylic leucate.

Since these reactions were thus expressed, zinc has come to be generally

* Proceedings of the Royal Society, vol. xii. p. 396.

regarded as a diatomic metal, a circumstance which has led us to study the action of zincethyl upon ethylic leucate, with a view to the more satisfactory elucidation of the above changes, which finally result in ethylic leucate. Assuming the diatomicity of zinc, which can now no longer be doubted, it is obvious that by the loss of one atom of ethyl, zincethyl will, like many other organo-metallic bodies, pass from a condition of perfect to one of partial saturation, in which it will play the part of a monatomic radical.

That zincethyl, in being acted upon by oxygen, passes through two distinct stages of change has been already indicated by one of us in describing the reactions of that body*; for when a current of dry oxygen is made to pass through an ethereal solution of zincethyl, dense white fumes continue to fill the atmosphere of the vessel, until about one-half of the total quantity of oxygen necessary for the complete oxidation of the zincethyl has been taken up. Then the white fumes entirely cease, showing the absence of free zincethyl, and at the same moment the liquid, which up to that time had remained perfectly transparent, begins to deposit a copious white precipitate, which continues to increase until the remaining half of the oxygen is absorbed. If the process of oxidation be arrested when the white fumes cease to be formed, the product effervesces violently when mixed with water, owing to the escape of hydride of ethyl; but when the oxidation is completed, the white solid mass produced consists chiefly of zincethylate, and does not in the slightest degree effervesce in contact with water. The two stages of this reaction depend essentially upon the successive linking of the zinc with the two atoms of ethyl by means of diatomic oxygen. The first stage of oxidation is expressed by the following equation:—

$$Zn'' \left\{ \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right. + O = Zn'' \left\{ \begin{matrix} C_2H_5 \\ O\,C_2H_5 \end{matrix} \right.$$

Zincethyl. Zincethylo-ethylate.

The zincethylo-ethylate thus formed is perfectly soluble in ether, and is instantly decomposed by water according to the following equation:—

$$Zn'' \left\{ \begin{matrix} C_2H_5 \\ O\,C_2H_5 \end{matrix} \right. + 2H_2O = Zn'' \left\{ \begin{matrix} OH \\ OH \end{matrix} \right. + \left. \begin{matrix} C_2H_5 \\ H \end{matrix} \right\} O + \left\{ \begin{matrix} C_2H_5 \\ H \end{matrix} \right.$$

Zincethylo-ethylate. Zinc hydrate. Alcohol. Ethylic hydride.

Treated with dry oxygen, zincethylo-ethylate, in ethereal solution, absorbs a second atom of that element, and it is this further absorption that constitutes the second stage above referred to, resulting in the production of ethylate of zinc,

$$Zn'' \left\{ \begin{matrix} C_2H_5 \\ O\,C_2H_5 \end{matrix} \right. + O = Zn'' \left\{ \begin{matrix} O\,C_2H_5 \\ O\,C_2H_5 \end{matrix} \right.$$

Wanklyn† was the first clearly to point out the probable existence of zincmonethyl, or rather its homologue zinc-monomethyl, indicating at the

* Phil. Trans. 1855, p. 268.

† Journal of Chem. Soc. 1861, p. 127.

same time its radical functions, when he ascribed to the crystalline compound obtained in the preparation of zincmethyl the formula

$$Zn_2' \left\{ \begin{matrix} CH_3 \\ I \end{matrix} \right.$$

In the same memoir he also represented this compound as the analogue of mercuric methiodide,

$$Hg'' \left\{ \begin{matrix} CH_3 \\ I \end{matrix} \right.$$

More recently Buttlerow† has prominently drawn attention to this behaviour of organo-zinc compounds, and has succeeded in obtaining zincmethylomethylate,

$$Zn'' \left\{ \begin{matrix} CH_3 \\ O\,CH_3 \end{matrix} \right.,$$

in a condition approaching to purity, by passing a stream of dry air through a solution of zincmethyl in methyl iodide. M. Buttlerow's success in obtaining this body and his failure in converting it into zincmethylate, are both probably due to the comparative insolubility of zincmethylo-methylate in methyl iodide, owing to which the first product of oxidation was, to a great extent, protected from the further action of oxygen. When, however, ether is used as the solvent of zincethyl, the oxidized product remains in solution until the first stage is passed, after which zincethylate is gradually precipitated until the second stage is completed. Indeed, as has been shown in the memoir above referred to (Phil. Trans. 1855, p. 268), the oxidation, instead of stopping at the first stage, proceeds even somewhat further than the second, and the product formed does not possess a composition in any degree approaching that which M. Buttlerow asserts it to have. This is evident from the following numbers, and from the circumstance that it does not effervesce in the slightest degree when mixed with water:—

	Percentage composition according to Buttlerow's formula $\left\{ \begin{matrix} C_2H_5\,Zn \\ C_2H_5 \end{matrix} \right.$	Percentage composition according to mean of analyses.
C	34·53	25·43
H	7·20	5·32
Zn	46·76	42·04
O	11·51	27·21
	100·00	100·00

The existence of monatomic organo-zinc radicals receives further support from the following experimental determinations, which also show the functions of such radicals in the formation of the ethers of the lactic series from ethylic oxalate.

When zincethyl is added to leucic ether previously cooled in a freezing mixture, each drop of the zinc compound, as it comes into contact with the ether, hisses like anhydrous phosphoric acid when dropped into water. Torrents of hydride of ethyl are evolved, and the mixture finally solidifies to a white tenacious mass, which fuses on the application of heat, and does

* Bulletin de la Soc. Chim. August 1864.

not distil below 100° C., at about which temperature a violent action sets in; a great quantity of gas is evolved, and the residue solidifies to a pitch-like mass, which, on treatment with water and subsequent distillation, yields about one-fourth of the leucic ether employed. If the above-mentioned white mass, instead of being heated, be mixed with water, it effervesces strongly, zinc hydrate is formed, and pure leucic ether separates in quantity nearly equal to that originally employed.

In a quantitative experiment 12·93 grms. of zincethyl were treated with leucic ether, excess being avoided; 15·67 grms. of leucic ether were required to saturate the above quantity of zincethyl, and the weight of hydride of ethyl evolved, which was carefully determined, amounted to 3·08 grms. These numbers closely agree with those deduced from the following equation:—

$$C_2\left\{\begin{matrix}(C_2H_5)_2\\ OH\\ O\\ O\,C_2H_5\end{matrix}\right. + Zn''\left\{\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right. = C_2\left\{\begin{matrix}(C_2H_5)_2\\ O\,Zn\,C_2H_5\\ O\\ O\,C_2H_5\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\},$$

Ethylic leucate. Zincmonethyl-ethylic leucate.

as seen from the following comparison:—

	Theoretical.	Experimental.
Leucic ether required to decompose 12·93 grms. of zincethyl	15·55 grms.	15·67 grms.
Weight of hydride of ethyl evolved ..	3·04 „	3·08 „

Zincmonethyl-ethylic leucate is a colourless viscous solid, soluble in ether, but apparently incapable of crystallization. It absorbs oxygen with avidity and in contact with water effervesces strongly, reproducing leucic ether according to the following equation:—

$$C_2\left\{\begin{matrix}(C_2H_5)_2\\ O\,Zn\,C_2H_5\\ O\\ O_2H_5\end{matrix}\right. + 2H_2O = C_2\left\{\begin{matrix}(C_2H_5)_2\\ OH\\ O\\ O\,C_2H_5\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\} + Zn''\left\{\begin{matrix}OH\\ OH\end{matrix}\right.$$

Zincomethyl-ethylic leucate. Ethylic leucate.

Zincmonethyl-ethylic leucate combines energetically with iodine; an ethereal solution of the latter added to it is almost instantaneously decolorized and a large quantity of iodide of ethyl is produced. In continuation of the above quantitative experiment the following results were obtained. The product of the action of 12·93 grms. of zincethyl upon 15·67 grms. of leucic ether decolorized an ethereal solution containing 23·75 grms. of iodine, the quantity required by the following equation being 25·04 grms.,

$$2C_2\left\{\begin{matrix}(C_2H_5)_2\\ O\,Zn\,C_2H_5\\ O\\ O\,C_2H_5\end{matrix}\right. + I_4 = C_4\left\{\begin{matrix}(C_2H_5)_4\\ O_2Zn\\ O\\ (O\,C_2H_5)_2\end{matrix}\right. + ZnI_2 + 2C_2H_5I.$$

Zincmonethyl-ethylic leucate. Zincoleucic ether.

It was obviously impossible to collect in a state of purity the iodide of ethyl thus set at liberty without considerable loss; but the quantity of the pure iodide actually obtained was 12 grms. The above equation requires 14·6 grms.

On the removal of ether and iodide of ethyl, the mixture of zincoleucic ether and iodide of zinc forms a transparent gummy mass easily soluble in ether, bisulphide of carbon, and caoutchoucin, but totally incapable of crystallizing from any of its solutions. All our attempts to separate these bodies have hitherto proved abortive, and it is by no means improbable that they are chemically combined.

The action of zincethyl upon ethylic leucate throws much light upon the production of the latter from zincethyl and ethylic oxalate, and scarcely leaves a doubt that, when zincethyl is added to ethylic leucate, there is reproduced the zinc compound from which the ethylic leucate was first formed. We may therefore express the two stages in the original production of ethylic leucate by the following equations:—

$$C_2\left\{\begin{matrix}O\\ O\,C_2H_5\\ \overline{O}\\ O\,C_2H_5\end{matrix}\right. + 2Zn''\left\{\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right. = C_2\left\{\begin{matrix}(C_2H_5)_2\\ OZnC_2H_5\\ \overline{O}\\ O\,C_2H_5\end{matrix}\right. + Zn''\left\{\begin{matrix}C_2H_5\\ O\,C_2H_5\end{matrix}\right.$$

Ethylic oxalate. Zincmonethyl-ethylic leucate. Zincethylo-ethylate.

$$C_2\left\{\begin{matrix}(C_2H_5)_2\\ OZnC_2H_5\\ \overline{O}\\ O\,C_2H_5\end{matrix}\right. + 2H_2O = C_2\left\{\begin{matrix}(C_2H_5)_2\\ OH\\ \overline{O}\\ O\,C_2H_5\end{matrix}\right. + Zn''\left\{\begin{matrix}OH\\ OH\end{matrix}\right. + \left\{\begin{matrix}C_2H_5\\ H\end{matrix}\right.$$

Zincmonethyl-ethylic leucate. Ethylic leucate. Zinc hydrate.

III. "Notes of Researches on the Acids of the Lactic Series.—No. IV. Action of Zinc upon Oxalic Ether and the Iodides of Methyl and Ethyl mixed in atomic proportions." By E. Frankland, F.R.S. and B. F. Duppa, Esq. Received February 2, 1865.

The reaction of zinc upon oxalic ether in the presence of iodide of amyl, the results of which we hope very shortly to have the honour of laying before the Royal Society, had led us to anticipate, that if an oxalate of one organic radical were treated with the iodide of another, one atom of diatomic oxygen in the oxalic ether would be replaced by two different monatomic radicals. This anticipation was not, however, realized, as we have already shown*, when the reaction was extended to a mixture of iodide of ethyl with oxalate of methyl, and iodide of methyl with oxalate of ethyl. In both these cases the radicals presented in the form of iodides were the

* Proceedings of the Royal Society, vol. xiv. p. 17.